



APPENDIX D

RE: U.S. Patent Application No. 08/961,956

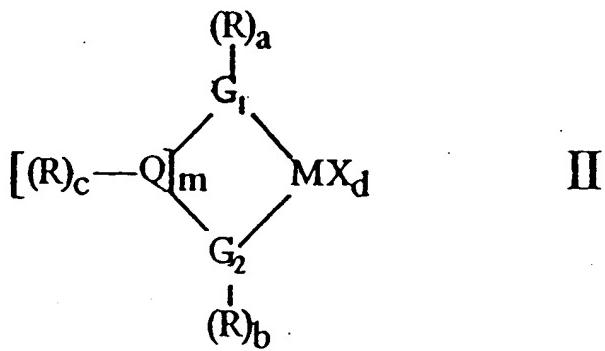
Applicant: Jose Sancho Royo, et al.

Title: "Catalytic Systems . . ."

Our Ref. No.: 616282-6/JP/B-3379

Please replace currently pending Claims 56-62, 65, 66, 69, 70, 75-80, and 84-89 with amended Claims 56-62, 65, 66, 69, 70, 75-80, and 84-89, which are set forth below.

Claim 56. (amended once) A catalyst for polymerization of alpha-olefins, wherein the catalyst comprises a cocatalyst and a catalyst component, wherein the catalyst component comprises a metallocene complex and a support, wherein the metallocene complex is supported on the support, wherein the metallocene complex is defined by formula I or II:



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wherein:

R groups are equal to or different from each other; each R is independently hydrogen or a radical containing from 1 to 20 carbon atoms; each R optionally contains a heteroatom selected from the group consisting of boron, germanium, tin, lead, and elements from groups 15 and 16 of the periodic table of the elements; at least one R group in the formula I and at least one R group in the formula II contain an OSiR^m₃ group, wherein R^m is selected from the group consisting of: linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl;

Q is selected from the group consisting of: boron and elements from groups 14 and 16 of the periodic table; when m > 1, Q groups are equal to or different from each other; free valences of every Q are filled with the R group or groups; two R groups optionally are bonded to form a ring having from 5 to 8 atoms, wherein the ring having from 5 to 8 atoms is directly bonded to Q; m is an integer ranging from 1 to 4;

the G groups in the formula I are equal to or different from each other; the G groups, G₁, and G₂ are each independently a cyclic organic group bonded to M through a π bond, a cyclopentadienyl ring that optionally is fused with one or more other rings, or an atom selected from the group consisting of elements from groups 15 and 16 of the periodic table; wherein at least one G group in the formula I is the cyclopentadienyl ring that optionally is fused with one or more other rings; wherein the R group that contains the OSiR^m₃ group in the formula I is directly bonded to the cyclopentadienyl ring that optionally is fused with

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one or more other rings; wherein in the formula II, G₁ or G₂ is the cyclopentadienyl ring that optionally is fused with one or more other rings; wherein in the formula II, the R group that contains the OSiR₃ group is directly bonded to Q or to the cyclopentadienyl ring that optionally is fused with one or more other rings;

M is a metal selected from the group consisting of: elements from groups 3, 4, and 10 of the periodic table, lanthanides, and actinides;

X groups are equal to or different from each other; X is selected from the group consisting of: halogen, hydrogen, OR'', N(R'')₂, C₁-C₂₀ alkyl, and C₆-C₂₀ aryl; wherein R'' is selected from the group consisting of: linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl;

x is an integer greater than or equal to 1, y is an integer greater than or equal to 2 in such a way that x + y = 3, 4, 5, or 6;

d is an integer ranging from 0 to 2; and a, b and c are integers from 0 to 10 in such a way that a + b + c ≥ 1; wherein the metallocene complex is supported on the support by means of a bond resulting from a reaction of the OSiR₃ group of the metallocene complex with a reactive group on a surface of the support; and wherein the OSiR₃ group is not directly bonded to Q when Q contains Si.

Claim 57. (amended once) A catalyst as claimed in Claim 56 wherein in the formula I and the formula II each R is

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independently selected from the group consisting of: hydrogen, linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl; wherein optionally each R group contains a heteroatom selected from the group consisting of: boron, germanium, tin, lead, and elements of groups 15 and 16 of the periodic table of the elements; and wherein at least one R group in the formula I and at least one R group in the formula II contain the OSiR"₃ group.

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Claim 58. (amended once) A catalyst as claimed in Claim 56 wherein in the formula I and the formula II M is selected from the group consisting of: Ti, Zr, and Hf.

Claim 59. (amended once) A catalyst as claimed in Claim 56 wherein in the formula I and the formula II the R group that contains the group OSiR"₃, is selected from the group consisting of: -CH₂-CH₂-OSiMe₃, -CH₂-CH₂-CH₂-OSiMe₃, -CH₂-O-CH₂-OSiMe₃, and -O-CH₂-CH₂-OSiMe₃.

Claim 60. (amended once) A catalyst as claimed in Claim 56 wherein in the formula I each G is independently cyclopentadienyl or indenyl; M is zirconium; **x** is 2; **y** is 2; each R is independently C₁-C₄ alkyl, wherein at least one hydrogen of one R is substituted with the OSiR"₃ group, wherein R" is selected from the group consisting of: Me, Et, and Pr.

Claim 61. (amended once) A catalyst as claimed in Claim 57

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wherein in the formula II M is zirconium; G₁ and G₂ are each independently cyclopentadienyl or indenyl; each R is independently hydrogen or a C₁-C₄ alkyl wherein at least one hydrogen of one R is substituted with the OSiR"₃ group, wherein R" is selected from the group consisting of: methyl, ethyl, and propyl; and wherein if [(R)_c-Q]_m does not contain the OSiR"₃ group, then [(R)_c-Q]_m is H₂C-CH₂, CRH-CH₂, RHC-SiR'₂, R₂C-SiR'₂, or SiRR', wherein R' is selected from the group consisting of linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl.

W/C
Claim 62. (Amended once) A catalyst as claimed in Claim 57 wherein in the formula II M is titanium; wherein G₂ is an oxygen or a nitrogen atom; wherein G₁ is a cyclopentadienyl, indenyl or fluorenlyl ring; and wherein if [(R)_c-Q]_m does not contain the OSiR"₃ group, then [(R)_c-Q]_m is H₂C-CH₂, CRH-CH₂, RHC-SiR'₂, R₂C-SiR'₂, or SiRR', wherein R' is selected from the group consisting of linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl.

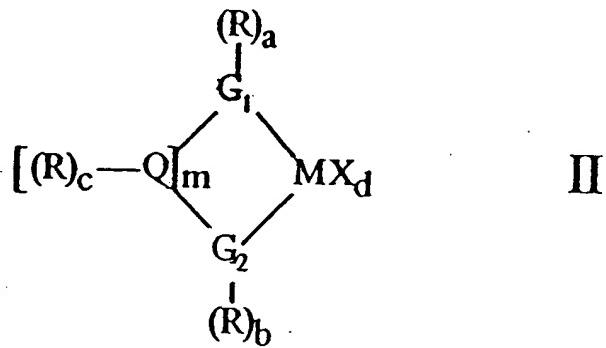
Claim 65. (amended once) A process for preparing a catalyst as claimed in Claim 56, wherein the process comprises the following steps:

- (a) impregnation on a support, under anhydrous conditions

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and an inert atmosphere at a temperature between -20°C and 90°C, of a solution comprising at least one metallocene complex and a cocatalyst, wherein the metallocene complex is defined by formula I or II

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wherein:

R groups are equal to or different from each other; each R is independently hydrogen or a radical containing from 1 to 20 carbon atoms; each R optionally contains a heteroatom selected from the group consisting of boron, germanium, tin, lead, and elements from groups 15 and 16 of the periodic table of the elements; at least one R group in the formula I and at least one R group in the formula II contain an OSiR["]₃ group, wherein R" is selected from the group consisting of: linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl;

Q is selected from the group consisting of: boron and elements from groups 14 and 16 of the periodic table; when m > 1, Q groups are equal to or different from each other; free valences of every Q are filled with the R group or groups; two R groups optionally are bonded to form a ring having from 5 to 8 atoms, wherein the ring having from 5 to 8 atoms is directly bonded to Q; m is an integer ranging from 1 to 4;

the G groups in the formula I are equal to or different from each other; the G groups, G₁, and G₂ are each independently a cyclic organic group bonded to M through a π bond, a cyclopentadienyl ring that optionally is fused with one or more other rings, or an atom selected from the group consisting of elements from groups 15 and 16 of the periodic table; wherein at least one G group in the formula I is the cyclopentadienyl ring that optionally is fused with one or more other rings; wherein the R group that contains the OSiR["]₃ group in the formula I is directly bonded to the cyclopentadienyl ring that optionally is fused with

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one or more other rings; wherein in the formula II, G₁ or G₂ is the cyclopentadienyl ring that optionally is fused with one or more other rings; wherein in the formula II, the R group that contains the OSiR"₃ group is directly bonded to Q or to the cyclopentadienyl ring that optionally is fused with one or more other rings;

M is a metal selected from the group consisting of: elements from groups 3, 4, and 10 of the periodic table, lanthanides, and actinides;

X groups are equal to or different from each other; X is selected from the group consisting of: halogen, hydrogen, OR'', N(R'')₂, C₁-C₂₀ alkyl, and C₆-C₂₀ aryl; wherein R'' is selected from the group consisting of: linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl;

x is an integer greater than or equal to 1, y is an integer greater than or equal to 2 in such a way that x + y = 3, 4, 5, or 6;

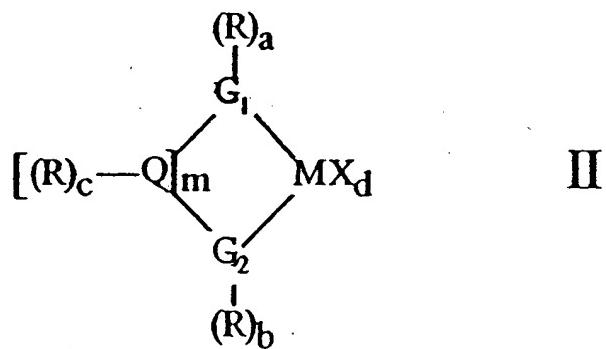
d is an integer ranging from 0 to 2; and a, b and c are integers from 0 to 10 in such a way that a + b + c ≥ 1; wherein the OSiR"₃ group of the metallocene complex reacts with a reactive group of the support to bond the metallocene complex to the support, thereby forming a resulting solid comprising the metallocene complex and the cocatalyst supported on the support; wherein the OSiR"₃ group is not directly bonded to Q when Q contains Si; and

- (b) filtration and washing the resulting solid from step (a) with a solvent comprising an aliphatic hydrocarbon or an aromatic hydrocarbon.

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Claim 66. (amended once) A process for preparing a catalyst as claimed in Claim 56, wherein the process comprises the following steps:

- (a) depositing at least one metallocene complex and a cocatalyst on a support by using a solution comprising a solvent, the metallocene complex, and the cocatalyst, wherein the metallocene complex is defined by formula I or II:



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wherein:

R groups are equal to or different from each other; each R is independently hydrogen or a radical containing from 1 to 20 carbon atoms; each R optionally contains a heteroatom selected from the group consisting of boron, germanium, tin, lead, and elements from groups 15 and 16 of the periodic table of the elements; at least one R group in the formula I and at least one R group in the formula II contain an OSiR["]₃ group, wherein R" is selected from the group consisting of: linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl;

Q is selected from the group consisting of: boron and elements from groups 14 and 16 of the periodic table; when m > 1, Q groups are equal to or different from each other; free valences of every Q are filled with the R group or groups; two R groups optionally are bonded to form a ring having from 5 to 8 atoms, wherein the ring having from 5 to 8 atoms is directly bonded to Q; m is an integer ranging from 1 to 4;

the G groups in the formula I are equal to or different from each other; the G groups, G₁, and G₂ are each independently a cyclic organic group bonded to M through a π bond, a cyclopentadienyl ring that optionally is fused with one or more other rings, or an atom selected from the group consisting of elements from groups 15 and 16 of the periodic table; wherein at least one G group in the formula I is the cyclopentadienyl ring that optionally is fused with one or more other rings; wherein the R group that contains the OSiR["]₃ group in the formula I is directly bonded to the cyclopentadienyl ring that optionally is fused with

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one or more other rings; wherein in the formula II, G₁ or G₂ is the cyclopentadienyl ring that optionally is fused with one or more other rings; wherein in the formula II, the R group that contains the OSiR"₃ group is directly bonded to Q or to the cyclopentadienyl ring that optionally is fused with one or more other rings;

M is a metal selected from the group consisting of: elements from groups 3, 4, and 10 of the periodic table, lanthanides, and actinides;

X groups are equal to or different from each other; X is selected from the group consisting of: halogen, hydrogen, OR'', N(R'')₂, C₁-C₂₀ alkyl, and C₆-C₂₀ aryl; wherein R'' is selected from the group consisting of: linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl;

x is an integer greater than or equal to 1, y is an integer greater than or equal to 2 in such a way that x + y = 3, 4, 5, or 6;

d is an integer ranging from 0 to 2; and a, b and c are integers from 0 to 10 in such a way that a + b + c ≥ 1; wherein the OSiR"₃ group of the metallocene complex reacts with a reactive group of the support to bond the metallocene complex to the support, thereby forming a resulting solid comprising the metallocene complex and the cocatalyst supported on the support; wherein the OSiR"₃ group is not directly bonded to Q when Q contains Si;

- (b) eliminating the solvent; and
- (c) bringing the resulting solid to a temperature between 25 and 150°C.

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Claim 69. (amended once) A catalyst according to Claim 57, wherein in the formula I and the formula II M is selected from the group consisting of: Ti, Zr, and Hf.

Claim 70. (amended once) A catalyst according to Claim 59, wherein in the formula I and the formula II M is selected from the group consisting of: Ti, Zr, and Hf.

Claim 75. (amended once) A process as claimed in Claim 65 wherein in the formula I and the formula II each R is independently selected from the group consisting of: hydrogen, linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl; wherein optionally each R group contains a heteroatom selected from the group consisting of: boron, germanium, tin, lead, and elements of groups 15 and 16 of the periodic table of the elements; and wherein at least one R group in the formula I and at least one R group in the formula II contain the OSiR"₃ group.

Claim 76. (amended once) A process according to Claim 65 wherein in the formula I and the formula II M is selected from the group consisting of: Ti, Zr, and Hf.

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Claim 77. (amended once) A process according to Claim 65 wherein in the formula I and the formula II the R group that contains the group OSiR["]₃ is selected from the group consisting of: -CH₂-CH₂-OSiMe₃, -CH₂-CH₂-CH₂-OSiMe₃, -CH₂-O-CH₂-OSiMe₃, and -O-CH₂-CH₂-OSiMe₃.

Claim 78. (Amended once) A process according to Claim 65 wherein in the formula I each G is independently cyclopentadienyl or indenyl; M is zirconium; **x** is 2; **y** is 2; each R is independently C₁-C₄ alkyl, wherein at least one hydrogen of one R is substituted with the OSiR["]₃ group, wherein R" is selected from the group consisting of: Me, Et, and Pr.

Claim 79. (amended once) A process according to Claim 75 wherein in the formula II M is zirconium; G₁ and G₂ are each independently cyclopentadienyl or indenyl; each R is independently hydrogen or a C₁-C₄ alkyl wherein at least one hydrogen of one R is substituted with the OSiR["]₃ group, wherein R" is selected from the group consisting of: methyl, ethyl, and propyl; and wherein if [(R)_c-Q]_m does not contain the OSiR["]₃ group, then [(R)_c-Q]_m is H₂C-CH₂, CRH-CH₂, RHC-SiR'₂, R₂C-SiR'₂, or SiRR', wherein R' is selected from the group consisting of linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl.

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Claim 80. (amended once) A process according to Claim 65 wherein in the formula II M is titanium; wherein G₂ is an oxygen or a nitrogen atom; wherein G₁ is a cyclopentadienyl, indenyl or fluorenyl ring; and wherein if [(R)_c-Q]_m does not contain the OSiR"₃ group, then [(R)_c-Q]_m is H₂C-CH₂, CRH-CH₂, RHC-SiR'₂, R₂C-SiR'₂, or SiRR', wherein R' is selected from the group consisting of linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl.

Claim 84.. (amended once) A process as claimed in Claim 66 wherein in the formula I and the formula II each R is independently selected from the group consisting of: hydrogen, linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl; wherein optionally each R group contains a heteroatom selected from the group consisting of: boron, germanium, tin, lead, and elements of groups 15 and 16 of the periodic table of the elements; wherein at least one R group in the formula I and at least one R group in the formula II contain the OSiR"₃ group.

Claim 85. (amended once) A process according to Claim 66 wherein in the formula I and the formula II M is selected from the group

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consisting of: Ti, Zr, and Hf.

Claim 86. (amended once) A process according to Claim 66 wherein in the formula I and the formula II the R group that contains the group OSiR"₃ is selected from the group consisting of: -CH₂-CH₂-OSiMe₃, -CH₂-CH₂-CH₂-OSiMe₃, -CH₂-O-CH₂-OSiMe₃, and -O-CH₂-CH₂-OSiMe₃.

Claim 87. (Amended once) A process according to Claim 66 wherein in the formula I each G is independently cyclopentadienyl or indenyl; M is zirconium; **x** is 2; **y** is 2; each R is independently C₁-C₄ alkyl, wherein at least one hydrogen of one R is substituted with the OSiR"₃ group, wherein R" is selected from the group consisting of: Me, Et, and Pr.

Claim 88. (amended once) A process according to Claim 84 wherein in the formula II M is zirconium; G₁ and G₂ are each independently cyclopentadienyl or indenyl; each R is independently hydrogen or a C₁-C₄ alkyl wherein at least one hydrogen of one R is substituted with the OSiR"₃ group, wherein R" is selected from the group consisting of: methyl, ethyl, and propyl; and wherein if [(R)_c-Q]_m does not contain the OSiR"₃ group, then [(R)_c-Q]_m is H₂C-CH₂, CRH-CH₂, RHC-SiR'₂, R₂C-SiR'₂, or SiRR', wherein R' is selected from the group consisting of linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀

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alkylaryl, and branched C₇-C₂₀ alkylaryl.

Claim 89. (amended once) A process according to Claim 66 wherein in the formula II M is titanium; wherein G₂ is an oxygen or a nitrogen atom; wherein G₁ is a cyclopentadienyl, indenyl or fluorenyl ring; and wherein if [(R)_c-Q]_m does not contain the OSiR"₃ group, then [(R)_c-Q]_m is H₂C-CH₂, CRH-CH₂, RHC-SiR'₂, R₂C-SiR'₂, or SiRR', wherein R' is selected from the group consisting of linear C₁-C₂₀ alkyl, branched C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, linear C₇-C₂₀ alkenyl, branched C₇-C₂₀ alkenyl, linear C₇-C₂₀ arylalkyl, branched C₇-C₂₀ arylalkyl, linear C₇-C₂₀ arylalkenyl, branched C₇-C₂₀ arylalkenyl, linear C₇-C₂₀ alkylaryl, and branched C₇-C₂₀ alkylaryl.